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PHOTOCONDUCTIVE CELLS

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/Figures referred to are appended./

(Author's Abstract: In connection with the progress attained in the study of the properties of lead sulfide photoconductive cells, interest in this type of photocell has increased considerably. A number of articles describing the properties of various types of photoconductive cells have appeared in scientific periodical literature. In addition to a review of photoconductive cells, this article contains a description of a new type of photoconductive cell developed by the Leningrad Physicotechnical Institute, using synthetic bismuth sulfide, whose photoelectric properties are better in a number of ways than those of presently known types of photoconductive cells.)

The photoconductive effect is an increase in conductance, observed in many insulating or semiconducting substances, under the absorption of luminous energy, X-rays, or corpuscular rays and under irradiation by electrons of medium or high velocity. The applicability of a certain material for practical use is determined by a number of factors i.e., the integral and spectral sensitivity, stability in operation, inertia, temperature dependence, etc. The increase in conductance under the action of light takes place gradually and finally reaches a limiting value, which depends on the temperature, applied voltage, light intensity, wave length of the incident light, and type of semiconductor. Thus, photoconductive cells are basically inertial devices. This inertia is very great in selenium and much less in lead sulfide, where the photoeffect is almost instantaneous in the audio-frequency range. Other materials are intermediate between selenium and lead sulfide with respect to inertia. The inertia arises because the photoconductive effect in most substances is provided mainly

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by secondary effects which develop in a semiconductor under the action of light and the potential difference applied. These secondary effects are much more intense than the primary effects in most cases.

Our knowledge of the photoconductive effect has reached a level permitting the development of a number of new photoconductive cells, which have been successfully used for practical purposes.

The operation of photoconductive cells can be described in the following manner: Under an applied voltage, a current flows in a photoconductive cell in darkness. The current increases under illumination. The difference between the dark current and the current under illumination is called the photocurrent. Both the light and dark currents are governed by Ohm's law within certain limits. The sensitivity of photoconductive cells is therefore a function of the applied voltage. The maximum voltage for which Ohm's law holds depends on the type of photoconductive cell (or, more accurately, the type of semiconductor) and on the magnitude of the dark current. Generally, the larger the dark resistance, the greater the voltage that can be applied to the cell. Unstable behavior and the development of irreversible changes because of heating set an upper limit to the applied voltage in each particular case.

The light current or photocurrent in most photoconductive cells is not proportional to the luminous flux because a considerable part of the photocurrent is the secondary current, which is not directly connected with the absorption of light. For present types of photoconductive cells, the relationship of photocurrent to luminous flux is satisfactorily described by the formula $\Delta i = AE^x$, where Δi is the photocurrent, E is the luminous flux, A is a proportionality constant dependent on the type and construction of photoconductive cell, and x is an exponent less than unity. This equation reveals the important fact that the sensitivity of photoconductive cells increases with a decrease of luminous flux and vice versa.

The integral sensitivity of photoconductive cells reaches very high values and considerably exceeds the sensitivity of both barrier-layer photocells and photoemissive cells. Characteristic sensitivities for each type of photoconductive cell are included in this article. As was noted, the sensitivity is determined by the applied voltage.

The spectral sensitivity of photoconductive cells is characteristic of the material used in them. In general, the sensitivity of this type of photoelectric device includes corpuscular rays (alpha and beta particles) and X-rays, as well as the ultraviolet, visible, and infrared regions of the spectrum. In addition, the conductance of a number of semiconductors and insulators increases when they are irradiated by medium-speed electrons. Thus, photoconductive cells have an extremely wide field of application with respect to spectral properties.

The effects of inertia, loss of sensitivity, fatigue, and temperature dependence have been studied thoroughly for selenium, in which all of these effects are quite sharply defined. The thalofides which have appeared recently are to a certain degree free from a number of these defects.

The types of photoconductive cells which have appeared very recently are free to a still greater degree of the defects listed above. In addition, experimental methods have been found to eliminate or sharply reduce the strong dependence of photocurrent and resistance on temperature which is inherent in this class of photocells. Thus, photoconductive cells can now be used for many practical purposes. The main comparative advantages of photoconductive cells are high sensitivity, simple production technology, feasibility of mass production, and small size.

Selenium Photoconductive Cells (Se)

Selenium photoconductive cells were the first photoelectric device to be used in engineering. Their production technology is quite simple and their photoelectric properties fairly good, but unfortunately, no methods have been found to stabilize their properties, and thus at present they are of interest only from the historical standpoint.

Modern photoconductive cells are considerably better than selenium cells in a number of properties. However, according to published data, their spectral sensitivity in the ultraviolet region has not been surpassed. Accordingly, continuation of work on the stabilization of the properties of selenium photoconductive cells is very desirable.

The distinguishing feature of the electric properties of selenium cells is the deviation of both the dark and light currents from Ohm's law. A great many works have been published on the production technology, properties, and electrical characteristics of selenium cells [1, 2].

Thalofides (Tl_2S)

The outstanding photoelectric properties of thallous sulfide in combination with oxygen were discovered in 1917 [3]. Until recently, thalofides were the only type of photoconductive cells used in engineering. Details on the production technology of thalofides were first published in the USSR by A. A. Sivkov in 1938[4]. The sensitivity of these photoconductive cells, measured at a luminous flux of one lux, reaches 2.5 amperes per lumen [5]. Their spectral sensitivity extends from 300 to 1,200 $m\mu$, with a maximum at about 1,000 $m\mu$. They operate at voltages of from 30 to 60 volts.

The major defects of thalofides are considerable temperature dependency, inertia, fatigue, and irreversible loss of sensitivity when exposed to short-wave light, making it necessary to cover them with a red filter. Since thalofides were the only photoconductive cells suitable for use in engineering, a great deal of experimental work has been done with them to improve their qualities and simplify their production technology. This work has produced good results. In 1946, two extensive articles were published on the comprehensive study of the photoelectric properties of thallous sulfide [6, 7]. This study included careful investigations which revealed for the first time the mechanism of the photoconductive effect. An article giving a detailed description of thallous sulfide cells, their design, application, etc., was published in 1947[8]. According to Hewlett, the author of the article, the new photoconductive cells were free from some of the defects noted above.

It should be noted that the light-sensitive layer is placed in a vacuum in thalofides.

Lead Sulfide Photoconductive Cells (PbS)

Lead sulfide cells, which have both high integral sensitivity and an extraordinarily wide range of spectral sensitivity, are a most important accomplishment of recent work on the photoeffect. The first brief articles on these photoconductive cells appeared in 1946[9, 10].

According to published data[11, 12], lead sulfide cells are produced by depositing lead sulfide on a glass surface by evaporation in a vacuum or by a chemical method. The layer is heat treated in an oxygen atmosphere.

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A long article was published in 1948 on the structure of the photosensitive PbS and PbSe layers and the mechanism of the photoconductive effect in them(13).

There is no definite data in published literature on the magnitude of the integral sensitivity of lead sulfide cells. According to some information, however, their sensitivity reaches 6-10 amperes per watt of radiant energy. This value was apparently obtained with the photocell at low temperature. It should be noted that the sensitivity of all photoconductive cells increases considerably with a decrease of temperature. For example, the sensitivity of PbS increases 100-fold in the transition from room temperature to the temperature of dry ice (-60°C)(10). Specially designed photoconductive cells have been built which permit one to maintain the light-sensitive layers at the temperature of dry ice or liquid air during operation.

The sensitivity of PbS photoconductive cells built in the Leningrad Physicotechnical Institute (LFTI) of the Academy of Sciences USSR reaches 0.15 ampere per watt of incident energy at room temperature and a light-source temperature of 2,848° K.

The typical spectral distribution of lead sulfide photoconductive cells is given in Figure 1 (curve 1). Here, as in the other diagrams, the sensitivity is given for unit incident energy. With a decrease in temp rature, the red cutoff is shifted toward the longer wave lengths(14).

A notable feature of these cells is the low inertia of the photoeffect. According to published data, the magnitude of the inertial effect is apparently dependent on the production technology. One of the first papers on these cells, for example, stated that the output decreased by 20% in changing from a frequency of 90 cps to 900 cps(10). In another work(9), it was stated that the photoeffect was instantaneous up to 5,000 cps.

The nature of the frequency dependency of lead sulfide cells produced in the LFTI is shown in Figure 2. The frequency characteristics of selenium cells and thalofides, borrowed from literature, are also shown in this figure for comparison. As Figure 2 shows, the frequency dependency of lead sulfide cells is immeasurably better than that of the other types.

The frequency response of lead sulfide cells was recorded in the laboratory of the Leningrad "Kinap" plant. The LFTI, together with the plant, installed these photoconductive cells for experimental use in the sound-reproducing equipment of Leningrad theaters. They replaced the cesium gas-filled photocells (TsG-3, TsG-4) ordinarily used in this equipment. The first results showed the marked advantages of using lead sulfide cells for sound-reproduction purposes. The sensitivity was increased considerably and the quality of reproduction improved. Since the production technology of these cells is quite simple and does not require any expensive or scarce materials, it is obvious that their introduction into motion-picture engineering will result in considerable savings.

The remarkable properties of lead sulfide photoconductive cells will probably permit their extensive use in technical equipment and as an experimental tool in the laboratory, especially in work in the near infrared region of the spectrum.

These cells are very good with regard to stability. To illustrate, data obtained from one cell which was continuously illuminated at 500 lux with a voltage of 12 v on it and a resistance connected in series is given in the following table.

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Table 1

Time (hr)	I_{dark} (μa)	I_{light} (μa)	Δi (μa)	Time (hr)	I_{dark} (μa)	I_{light} (μa)	Δi (μa)
0	91.5	121.5	30	192	80	111	31
24	88.5	121.0	32.5	240	83	112.5	29.5
72	77	110	33	288	84	112.5	28.5
96	82	112	30	360	91	120	29
120	86	117	31	432	92	121	29
144	84	113	29	528	94	123	29
168	80	111	31				

The above data was obtained with a cell located in air without any special protective measures except for a transparent layer of varnish over the light-sensitive surface.

The changes in current are probably due to the temperature dependency, which ranges from 2 to 5% per 1° C in these cells according to our measurements.

The sensitivity of lead selenide and lead telluride photoconductive cells extends farther into the infrared[16]. The photoeffect in lead selenide has a red cutoff at 5.5 μ. There are two maxima, one at 2.5 and one at 3.5 μ. The spectral sensitivity of PbSe photoconductive cells is given in Figure 1 (curve 2). It is known that they operate effective at low temperatures. The integral sensitivity of these cells is considerably less than that of lead sulfide cells, being only about 0.1 ampere per watt of radiant energy.

One source[17] states that the sensitivity of lead telluride is 100 times that of a thermocouple at its maximum, i.e., is comparable with that of lead sulfide. The sensitivity of PbTe is greater than the sensitivity of a thermocouple up to 4.6 μ. The distinguishing feature of PbTe cells is the fact that they operate only at the temperature of liquid air.

The method of producing these cells is apparently about the same as that used for obtaining sensitive PbS layers.

Silicon Photoconductive Cells

A considerable photoeffect has been discovered in silicon deposited on a heated porcelain or quartz surface[18]. The spectral sensitivity of these cells has a maximum at 0.84-0.86 μ: the long-wave cutoff is at 1.2-1.5 μ. The general form of the spectral response is shown in Figure 3.

The distinguishing feature of silicon cells, according to published data[18], is the linear relationship between photocurrent and illumination. There is also a linear relationship up to 200 v/cm between applied voltage and dark and light currents.

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The frequency response was not given in the description of these cells, but it was stated that it is considerably better than that of selenium cells. Silicon cells are very stable; heating to red heat in an oxygen-gas flame does not produce irreversible changes in the properties of the cell. Neither are there any changes under prolonged illumination by direct sunlight. Data on the sensitivity of silicon photoconductive cells is given in Table 2.

Table 2

Sensitivity at 200 v/cm (ma/lumen)	Change of Dark Current per Lumen (%)	I_{light}/I_{dark} per Lumen	I_{light}/I_{dark} at 127 ft-candles
55.8	1,720	18.2	2.007
74	1,890	19.9	2.004
34	1,040	11.4	2.193

Cadmium-Sulfide Photoconductive Cells

Artificially obtained crystals of cadmium sulfide exhibit a photoeffect in the visible region and are also sensitive to X-rays and corpuscular radiation[19]. Compounds of cadmium wi[illegible] selenium (CdSe) and tellurium (CdTe) also exhibit a photoconductive effect. Cells of these materials are monocrystals grown by the interaction of cadmium vapor with H_2S, H_2Se, or H_2Te at high temperature in a special furnace. If the proper conditions are selected, monocrystals of considerable size, e.g., up to 1-2 sq cm, can be grown. Aluminum electrodes separated by 0.2-0.3 mm are deposited on the surface of these monocrystals by evaporation in a vacuum.

Cadmium sulfide photocells differ from other types in their spectral sensitivity, which has a sharply defined maximum around 530 mμ. The type of spectral sensitivity and its dependence on applied voltage is shown in Figure 4.

The magnitude of the integral sensitivity and the general nature of the change of resistance can be judged from the following example[19]: the photocell consists of a crystal of dimensions 3 x 10 x 0.1 mm with a sensitive area of 0.2 x 10 mm. Under illumination by a 10-watt incandescent lamp with a lens of diameter 5 cm and a focal length of 5 cm and an applied voltage of 10 v, the resistance drops from more than $10^8\,\Omega$ to $10^4\,\Omega$.

Cadmium sulfide photocells are very stable. Their properties do not change over a period of years if the load does not exceed 1 mw/sq mm. According to the published data, the frequency response, even though it drops at 10 kc, is still better than that of known photoconductive cells. The data given in Table 3 illustrates the nature of the photoconductance for X-rays and corpuscular radiation.

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Table 3

Radiation	Energy Incident on Crystal per Second	Field Intensity (v/cm)	Current (a)
X-ray tube, 30 kv, 15 ma	1×10^8 quanta	2,500	15×10^{-6}
Gamma rays, 10 mg of Ra 25 cm from crystal	2×10^6 quanta	2,500	2×10^{-7}
Alpha rays, Ra preparation, radiation 10^3-10^4 alpha particles from one sq cm per sec	1×10^3 particles	2,500	7.5×10^{-8}
Beta-particles, 10 mg Ra 5 cm from crystal	1×10^4 particles	2,500	1×10^{-5}

Only data pertaining to the spectral sensitivity has been given for CdSe and CdTe. For CdSe, the sensitivity maximum occurs at 600 μ [probably should be mμ]; for CdTe, this lies at 620 mμ.

In completing this review of photoconductive cells known from published literature, we note that of all the photoconductive cells discussed, cadmium sulfide cells are the best with regard to change of resistance under illumination.

Bismuth Sulfide Photoconductive Cells (Bi_2S_2)

The good photoelectric properties of bismuth sulfide in the form of natural crystals have become known only comparatively recently. In 1948, bismuth sulfide photoconductive cells were produced in the LFTI. Photographs of these cells are shown in Figure 5. The new photoconductive cells have the following properties:

The sensitivity reaches a value of 80 ma/lumen for a surface illumination of 100 lux and an applied voltage of 80 v. The sensitivity, measured at one lux, is about 400 ma/lumen. If the sensitivity is expressed in amperes per watt of incident energy, a value of 8.35 a/w is obtained. In determining the sensitivity, a lamp with a color temperature of 2,848° K was used.

Bismuth sulfide cells differ from lead sulfide and thallium sulfide cells chiefly by the fact that their spectral sensitivity has a maximum in the visible region of the spectrum. From this standpoint, they are similar to selenium cells. The typical distribution of spectral sensitivity for bismuth sulfide photoconductive cells is shown in Figure 6.

The distinguishing feature of the light characteristics of the bismuth sulfide cells as compared with thalofides is the smoother transition from small to great illuminations. For example, if the sensitivity of thalofides is determined at one lux, it may be 2.5 a/lumen. If the sensitivity is determined at 100 lux, it may be only 0.16 a/lumen, i.e., only one fifteenth of the former figure (5). This ratio is about one fourth or one fifth for bismuth sulfide cells.

The frequency response of bismuth sulfide cells is considerably better than that of selenium and thallium cells.

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Bismuth sulfide cells are very stable since they are not damaged by the so-called "flashes" and do not exhibit irreversible loss of sensitivity when irradiated by light in various sections of the spectrum, as is true of thalofides.

It should not be considered that the characteristics cited above for bismuth sulfide cells are the best attainable. It is very probable that some of these characteristics can be improved considerably. Even in their present form, however, these cells can be used extensively in engineering.

The main field of application of the new photoconductive cells should be in photoelectric automatic control. The cells can also be used successfully in the ordinary circuits for controlling the grid potential of an electron tube. In addition, new potentialities have been revealed with the development of the photorelay, i.e., a combination of a photoconductive cell with an electromagnetic relay, which eliminates the need for electron tubes.

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/Appended figures follow./

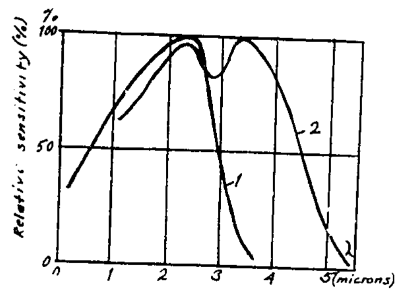

Figure 1. Spectral Sensitivity of Lead Sulfide (Curve 1) and Lead Selenide (2) Photoconductive Cells

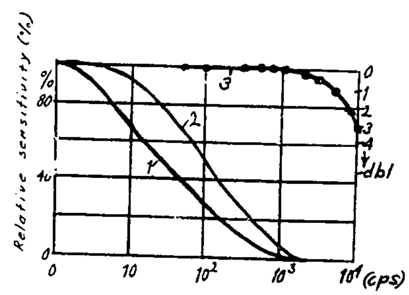

Figure 2. Frequency Responses of Selenium Cells (1), Thalofides (2), and Lead Sulfide Cells (3)

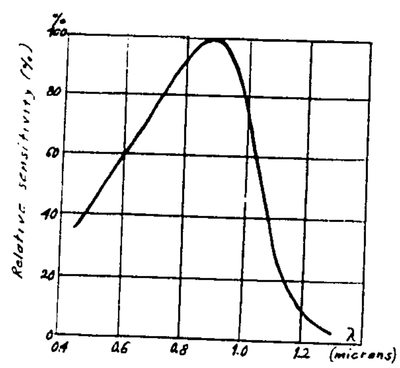

Figure 3. Distribution of Spectral Sensitivity of Silicon Cells

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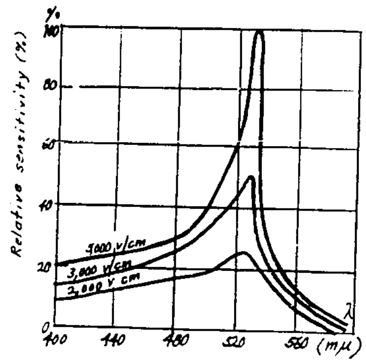

Figure 4. Spectral Sensitivity of Cadmium Sulfide in the Visible Part of the Spectrum for Various Electric Fields

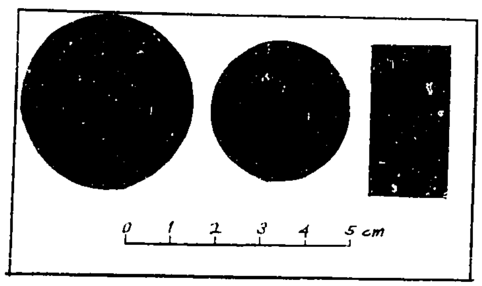

Figure 5. External View of Bismuth Sulfide Photoconductive Cells

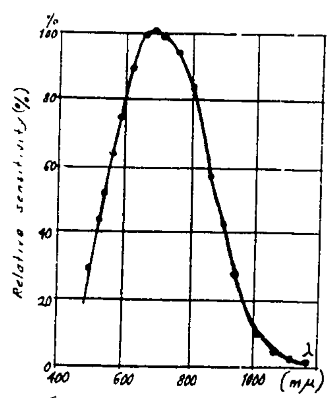

Figure 6. The Spectral Sensitivity of Bismuth Sulfide Photoconductive Cells

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